Current levels (2003-2004) of brominated flame retardants in feed and selected Norwegian seafood

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Introduction

Global use of brominated flame retardants (BFRs) has increased steadily since the 1970s, ironically, as a direct result of the phase-out of leaded gasoline to reduce pollution. Declining production of ethylene dibromide, a key ingredient in leaded gas used to reduce the build-up of lead in car engines, created a large excess in bromine production capacity that prompted new industrial uses for bromine. The shift to BFRs was also partly due to flammability standards imposed on plastic products, which are difficult to meet with the chlorinated flame retardants used previously. Today, more than 200,000 metric tons of BFRs are produced each year[1]. The BFRs are widely used in plastics, foams and textiles. The three major types of BFRs, in order of their current usage, include tetrabromobisphenol A (TBBP-A), hexabromocyclododecane (HBCD), and polybrominated diphenyl ethers (PBDEs). In Norway, the lower brominated PBDEs found in the commercial products of penta- and octa-BDE were banned as of July 2004. However, neither regulations on BFR levels in food, nor risk-based thresholds have been established by the European Union or the European Food Safety Authority (EFSA) respectively. Recent market basket studies have detected PBDEs in a wide range of food, including fish and other seafood species, and national food surveys have identified the diet as one of the main sources of human exposure to BFRs[2-4]. In Norway, seafood is the second largest export following oil. This study reports on the levels of 6 prominent PBDE congeners (PBDE-28, 47, 99, 100, 153, and 154) and total HBCD (sum of α, β, and γ isomers) found in a random selection of fish feeds and common seafood species collected in Norwegian food surveillance programs from 2003 and 2004.

Materials and Methods

*Samples:*Fish feed, oils, and seafood samples were collected byinspectors from the Norwegian Directorate of Fisheries in 2003 and 2004 from food surveillance programs on behalf of the Norwegian Food Safety Authority. Farmed Atlantic salmon (n=25 in 2003; n=17 in 2004), wild Atlantic salmon (n=9 in 2004), and mackerel (n=5 in 2003; n=24 in 2004) were filleted, skinned, and homogenized individually before analyses. Herring were collected from the North Sea region (n=25 in 2003; n= 25 in 2004) and southern coastal regions of Norway (n=25 in 2003; n=23 in 2004). Herring samples represented a pool of 5 fish/sample that had been filleted, but not skinned. Blue mussels were collected in southern coastal regions, and 25 specimens were used to create pooled samples (n=50 in 2003; n=33 in 2004). All samples were homogenized and stored at -20 °C in aluminium foil until analysis.

Sample Analysis: The gas chromatography with mass spectrometer negative-chemical ionization (GC/MS-NCI) methods, accredited according to European ISO 17025, for the determination of PBDEs (congeners 28, 47, 99, 100, 153, and 154) were based on the methods described previously[5,6]. In order to determine total HBCD, the GC program was adjusted such that the injection port was set to 225 °C, and the oven temperature was reduced to start at 45 °C to enable the recovery of total sum of HBCD isomers.Analyses were performed on a Thermo Finnigan Trace GC, coupled to a Trace DSQ mass spectrometer with helium (1.2 mL/minute) as the carrier gas. Splitless with surge injections of 1 mL were made by a Thermo Finnigan AS 3000 autosampler. The GC column was a 30 m x 0.25 mm i.d. (0.25-mm film thickness) RTX-5MS capillary column (Restek, Bellefonte, PA, USA). The mass spectrometer was operated in the NCI mode using methane (3.5 mL/min) as the reagent gas and the ion-source temperature was 230 °C. Selective ion monitoring of the two bromide ions at *m/z* 79 and 81 was used to detect PBDEs and HBCD. The instrument limit of quantitation was found to be 0.03 ng/g and 5.0 ng/g for PBDEs and HBCD, respectively. The response factors for all compounds were determined using quantitation standards (Cambridge Isotope Laboratories, Andover, MA, USA) with known amounts of target compounds and native PBDE internal standards. Quality assurance of the results was demonstrated as the laboratory used for the analyses regularly participates in international inter-laboratory trials of measurements of the compounds of interest, in-house control samples were analyzed together with the samples, and blank analyses were performed carrying out the entire

analytical procedure omitting only the sample.

Results and Discussion

Tables 1 and 2 show the results for primary PBDEs and total HBCD determined in fish feeds, oils used in feeds, and in selected Norwegian seafood species collected in 2003 and 2004. Table 1 shows the average levels of PBDEs in complete fish feeds of 2.7 ng/g and 3.0 ng/g in 2003 and 2004, respectively. Fish oil contained approximately 20-fold greater concentrations of PBDEs than found in vegetable oils used for feeds. Feed surveillance in 2004 included HBCD, however, only one fish oil sample had detectable levels, with a concentration of 7.6 ng/g. As previously observed by Hites et al., Table 2 shows farmed salmon have higher levels of PBDEs then do wild salmon[7]. Also, the mean levels of PBDEs in Table 2 show farmed salmon have increased slightly from 2003 to 2004. As with polychlorinated biphenyls (PCBs), it is likely that PBDEs and HBCD contamination in farmed Atlantic salmon comes via marine oils used in aquaculture feed[8]. The results in Table 1 demonstrate that fish feeds and fish oils can be a major source of PBDEs to farmed animals.

The average concentrations (Table 2) for the sum of PBDE congeners found in herring collected from the North Sea accounted for the lower range of concentrations compared to the higher levels found for herring collected in the more populated coastal regions southern Norway. While average PBDE levels in herring were somewhat lower than those observed in farmed Atlantic salmon, the levels of total HBCD observed in herring and farmed salmon were identical at 1.3 ng/g wet weight (wt). The concentrations of PBDEs in mackerel appear the same for 2003 and 2004 (Table 2), and only one sample had detectable levels of HBCD in 2004 at 1.2 ng/g wet wt. In blue mussels collected from different sampling sites, the average concentrations for PBDEs were higher by nearly 3-fold in 2004 as compared to 2003. For 2004, the levels of total HBCD isomers in blue mussels were equal to that of primary PBDEs (0.4 ng/g wet wt).

The congener profiles for the measured PBDEs here (data not shown), were similar to those reported previously, and indicate that PBDE 47, 99, and 100 are the most abundant congeners found, with PBDE 47 representing 60 to 70% of the total PBDEs observed[5]. Congener specific accumulation of PCBs in farmed Atlantic salmon has been studied previously, where preferential accumulation of non-ortho PCBs with tetra chlorine substitution was found over other non-ortho and mono-ortho substituted PCBs[9]. Since PBDE 47 is also a tetra substituted congener that is structurally similar to tetra-substituted non-ortho PCBs, similar mechanisms for PBDE 47 accumulation in seafood may also be present. While PBDE 209 was not measured in this and many other studies, due to its known degradation and extensive metabolism to lower PBDE congeners, it must be considered that break down products of PBDE 209 may be represented as the lower PBDEs generally reported[10-12]. The reactive flame retardant TBBP-A and isomeric forms of HBCD will be the focus of future surveillance programs, with the help of LC/MS/MS instrumentation and methods. Finally, as the toxicity of PBDEs is known to be additive to that of PCBs, it is likely that dual exposure to these contaminants, present with other similarly acting toxicants such as HBCD, may put both marine organisms and consumers at risk[13]. The replacement of fish oils with vegetable oils in complete animal feeding stuffs will significantly reduce exposure to brominated flame retardants occurring through the diet.

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Table 1. Concentrations (ng/g, mean* ±SD) of primary PBDEs from 2003 and 2004

representing fish feeds, and oils for use in feeds.

PBDEs	Feed	Feed	Fish oil	Vegetable oil
ng/g	2003 (n= 22)	2004 (n=10)	2004 (n=6)	2004 (n=7)
Mean ± SD	2.70 ± 1.92	3.04 ± 2.66	5.10 ± 8.45	0.24 ± 0.28
Range	0.64 - 7.88	0.55 - 8.96	1.14 - 8.45	0.12 - 0.87

*mean of the sum of 6 PBDE congeners (28, 47, 99, 100, 153, 154), mean values do not contain <*limit of quantitation results

Table 2. Sum of primary PBDE and total HBCD concentrations (ng/g, mean* ±SD, ranges) observed in 2003 and 2004 seafood surveillance programs for the Norwegian Food Safety Authority. The number of samples for each species is described in the Materials and Methods section.

Seafood Species	**PBDEs**	**PBDEs**	**Total HBCD**
	2003	**2004**	**2004**
	(ng/g wet weight)	(ng/g wet weight)	(ng/g wet weight)
Farmed Atlantic Salmon (*Salmo salar*)	2.33 ± 1.07 (1.10 – 4.50)	2.48 ±0.50 (1.90 – 3.40)	1.33 ± 0.33 (0.80 – 1.80)
WildAtlanticSalmon (*Salmo salar*)	Not Available	0.80 ± 0.20 (0.50 – 1.10)	Not determined
Herring (*Cupeaharengus*)	1.90 ± 0.82 (1.02 – 3.53)	1.93 ± 0.97 (0.60 – 3.76)	1.34 ± 0.67 (<0.63 – 2.75)
Mackerel (*Scomberscombrus*)	1.46 ± 0.23 (1.26 – 1.78)	1.44 ± 0.79 (0.59 – 3.54)	(<0.89 – 1.19)
Blue Mussels *(Mytilusedulis)*	0.15 ± 0.06 (0.06 – 0.25)	0.42 ± 0.37 (0.06– 1.60)	0.43 ± 0.17 (<0.17 – 0.87)

*mean of the sum of PBDE congeners (28, 47, 99, 100, 153, 154) and HBCD isomers (a,b,g); mean values do not include results found below the limits of quantitation.